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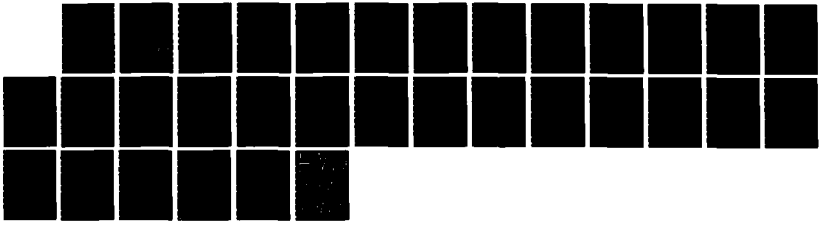

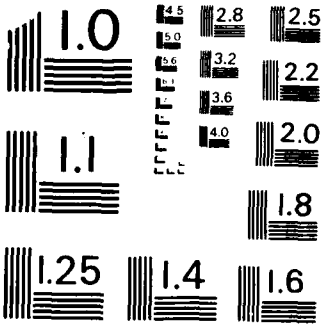

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Synthesis and Characterization of Liquid Crystalline Polysiloxanes Containing Benzyl Ether Mesogens

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ABSTRACT

Side chain liquid crystalline polysiloxanes were synthesized by the hydrosilation of poly(methylhydrosiloxane) with p-(1-undecenyl-11-oxy) benzyl ethers of: 4-cyanophenol (IM), 4-methoxyphenol (IIM), 4-cyano-4'-hydroxybiphenyl (IIIM), 4-methoxy-4'-hydroxybiphenyl (IVM) and 2-cyano-6-hydroxynaphthalene (VM). The phase behavior of both monomeric and polymeric liquid crystals was characterized by differential scanning calorimetry and optical polarization microscopy. IM is a monotropic liquid crystal, IIM is crystalline, IIIM and IVM are enantiotropic liquid crystals, while VM presents two virtual liquid crystalline transitions and crystalline polymorphism. All the synthesized polysiloxanes present enantiotropic smectic mesomorphism.

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Synopsis

Side chain liquid crystalline polysiloxanes were synthesized by the hydrosilation of poly(methylhydrosiloxane) with p-(1-undecenyl-11-oxy) benzyl ethers of: 4-cyanophenol (IM), 4-methoxyphenol (IIM), 4-cyano-4'-hydroxybiphenyl (IIIM), 4-methoxy-4'-hydroxybiphenyl (IVM) and 2-cyano-6-hydroxynaphthalene (VM). The phase behavior of both monomeric and polymeric liquid crystals was characterized by differential scanning calorimetry and optical polarization microscopy. IM is a monotropic liquid crystal, IIM is crystalline, IIIM and IVM are enantiotropic liquid crystals, while VM presents two virtual liquid crystalline transitions and crystalline polymorphism. All the synthesized polysiloxanes present enantiotropic smectic mesomorphism.

INTRODUCTION

In the past twenty-five years, the relationship between the chemical structure and the properties of low molecular weight liquid crystals underwent such a dramatic development, that in recent years organic chemists could safely state: "Contrary to the theoretician's belief, the constituent molecules of liquid crystals are neither rigid nor cylindrically symmetric" (1). This relationship has been extensively discussed and reviewed (1-10). The latest developments in the synthesis of low molecular weight liquid crystals include: aromatic and aliphatic heterocyclic mesogens, cycloaliphatic mesogens, as well as the replacement of the traditional rigid ester interconnecting group between either aromatic or cycloaliphatic units, by the flexible "ethyl" and "methyleneoxy" linkages.

Since 1978 when Ringsdorf and Finkelmann have introduced the spacer concept (11,12), the synthesis of side-chain liquid crystalline polymers became an active area of polymer chemistry. This field has been recently reviewed (13,14). Recently, we became interested in the synthesis of liquid crystalline polymers containing mesogenic units which present conformational isomerism. The first examples described by us refer to liquid crystalline polymers containing 1,4-disubstituted-2,5-dioxane based mesogens (15,16).

The goal of this paper is to present the synthesis and characterization of the first examples of liquid crystalline polymers containing benzyl ether based mesogens, i.e., side chain liquid crystalline polysiloxanes. Because of the free rotation around the ether bonds, these polymers represent the simplest class of liquid crystals containing mesogenic groups which present conformational isomerism.

EXPERIMENTAL

A. Materials

Poly(methylhydrosiloxane) ($\overline{Mn}$ = 4500 - 5000) was obtained from Petrarch Systems Inc., and used as received. 11-Undecan-1-ol, 4-methoxyphenol, 4-cyanophenol, 2-bromo-6-hydroxynaphthalene, 4,4'-di-hydroxybiphenyl and p-hydroxybenzaldehyde (Aldrich) were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon.

B. Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard unless noted. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. After the first heating scan, the sample was "annealed" at about 10°C above the isotropization temperature for 5-10 min. Under these registration conditions, beginning with the second heating and cooling scans all the DSC scans gave perfectly reproducible data. The transitions reported were read during the second or third heating and cooling scans unless otherwise specified. A Carl-Zeiss optical polarizing microscope (magnification: 100x) equipped with a Mettler

FP82 hot stage and a Mettler FP80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.

C. Synthesis of Monomers and Polymers

The synthesis of benzyl ether based monomers is outlined in Scheme 1.

11-Chloro-1-undecene

A mixture containing 34 g (0.2 mol) of 11-undecen-1-ol and 35.7 g (0.3 mol) of $SOCl_2$ was stirred for 3 hrs at 40°C. Excess $SOCl_2$ was distilled off and the resulting product was subjected to a fractional distillation (85°C/7 mm Hg) to yield 35 g of product. The purity of the resulted product was higher than 99% as determined by gas chromatography.

p-(1-Undecenyl-11-oxy)benzaldehyde

To a sodium ethoxide solution prepared by dissolving 1.15 g (0.05 mol) of cleanly cut sodium in 50 ml of absolute ethyl alcohol, 6.3 g (0.05 mol) of freshly distilled p-hydroxybenzaldehyde was added. The ethanol was completely evaporated on a rotovapor and the sodium salt of p-hydroxybenzaldehyde was isolated. The dried sodium salt was immediately dissolved into 50 ml of N-methyl-2-pyrrolidinone and 9.4 g (0.05 mole) of 11-chloro-1-undecene was added. The resulted solution was stirred at 110°C under a nitrogen atmosphere for 5 hrs, cooled, filtered to remove the obtained sodium chloride, and the solvent was removed in a rotovapor. The resulted oil was purified by column chromatography (silica gel, chloroform eluent) to yield 12.5 g (90%). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.29-2.02 (m, 16H, $-(\underline{CH}_2)-_8$, 3.94 (t, 2H, $-O\underline{CH}_2-$), 4.85 and 5.67 (m, 3H, $-\underline{CH}=\underline{CH}_2$), 6.83 and 7.62 (2d, 4 aromatic protons).

p-(1-Undecenyl-11-oxy)benzyl alcohol

A solution containing 1.70 g (0.045 mol) of $NaBH_4$ in 10 ml of 0.45N aqueous NaOH was added dropwise to a stirred mixture containing 12.5 g of p-(1-undecylenyl-11-oxy)benzaldehyde and 400 ml of methanol. The reaction mixture was stirred at room temperature for 1 hr. Half of the methanol was then evaporated and the solution was poured into water. The precipitated white solid was filtered, dried under vacuum, and recrystallized from n-hexane to yield 12 g (95%). mp = 55°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.31-2.07 (m, 16H, $-(CH_2)_8-$), 3.95 (t, 2H, $-OCH_2-$), 4.61 (s, 2H, $-Ph-CH_2-$), 4.94 and 5.77 (m, 3H, $-CH=CH_2$), 6.86 and 7.24 (2d, 4 aromatic protons).

p-(1-Undecenyl-11-oxy)benzyl chloride

p-(1-Undecenyl-11-oxy)benzyl alcohol (12 g, 0.043 mol) was dissolved in 150 ml methylene chloride and 6.2 g (0.052 mol) of $SOCl_2$ were added dropwise. After the addition was completed, the reaction mixture was stirred for 30 min, washed with water, 2% $NaHCO_3$ aqueous solution, water and dried over anhydrous sodium sulfate. The dried solution was passed through a silicagel column, and the solvent was evaporated to yield 12 g of an oily product (94%). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.31-2.06 (m, 16H, $-(CH_2)_8-$), 3.91 (t, 2H, $-OCH_2-$), 4.53 (s, 2H, $-Ph-CH_2Cl$), 4.94 and 5.76 (m, 3H, $-CH=CH_2$), 6.83 and 7.26 (2d, 4 aromatic protons).

4-Methoxy-4'-hydroxybiphenyl

4-Methoxy-4'-hydroxybiphenyl was synthesized as reported in a different publication from our laboratory (17).

4-Cyano-4'-hydroxybiphenyl

An improved synthesis of 4-cyano-4'-hydroxybiphenyl was recently

reported from our laboratory (16).

2-Cyano-6-hydroxynaphthalene

Copper (I) cyanide (6.71 g, 0.075 mol) was added to a solution containing 11.2 g (0.05 mol) of 2-bromo-6-hydroxynaphthalene in 50 ml of dry N-methyl-2-pyrrolidinone and refluxed for 1.5 hrs. The reaction mixture was cooled to 100°C, poured into a solution of iron (III) chloride (15.4 g) in water (25 ml) and concentrated hydrochloric acid (8.5 ml), and stirred at 60°C for 30 min. The obtained mixture was extracted with ethyl ether. The ether layer was treated with charcoal, dried over anhydrous sodium sulfate, and then evaporated to dryness. The obtained solid was recrystallized from water to yield 4.3 g (51%) crystals with mp = 163-165°C. ^{1}H-NMR (DMSO-d_6, δ, ppm): 3.43 (s, 1H, -OH), 7.28 to 8.43 (m, 6 aromatic protons).

p-(1-Undecenyl-11-oxy)benzyl ethers of 4-cyanophenol (IM), 4-methoxyphenol (IIM), 4-cyano-4'-hydroxybiphenyl (IIIM), 4-methoxy-4'-hydroxybiphenyl (IVM), and 2-cyano-6-hydroxynaphthalene (VM)

The benzyl ethers listed above were synthesized by the etherification of the corresponding sodium phenolate with p-(1-undecenyl-11-oxy)benzyl chloride. An example is presented below. 0.23 g (0.01 mol) of freshly cut sodium was dissolved in 50 ml of absolute ethyl alcohol. After the sodium was completely dissolved, 1.19 g (0.01 mol) of 4-cyanophenol was added all at once. The ethyl alcohol was removed by a rotovapor to form the sodium salt of 4-cyanophenol, and 50 ml of dried N-methyl-2-pyrrolidinone were added into the same flask. When the sodium salt was completely dissolved, 3.1 g (0.01 mol) of p-(1-undecenyl-11-oxy)benzyl chloride

was added to the reaction mixture. The reaction was stirred at 110°C under nitrogen atmosphere for 5 hr, cooled, and poured into water. The resulted precipitate was filtered, washed with dilute NaOH aqueous solution, water, and dried in vacuum. The product was recrystallized from methanol to yield 3.6 g (95%) of white crystals. Table I summarizes the chemical shifts for all synthesized compounds, while Table II presents the thermal transitions of the same compounds.

Dicyclopentadienylplatinum (II) chloride catalyst

The platinum catalyst was synthesized according to a literature procedure (18,19).

Synthesis of Polysiloxanes

The synthesis of liquid crystalline polysiloxanes is outlined in Scheme 2. A general synthetic procedure is described below. 1.0 g (10 mole % excess versus the Si-H groups present in polysiloxane) of the olefinic derivative was dissolved in 100 ml of dry, freshly distilled toluene together with the proper amount of polymethylhydrosiloxane. The reaction mixture was heated to 110°C under nitrogen, and 100 µg of dicyclopentadienylplatinum (II) chloride catalyst were then injected with a syringe as solution in methylene chloride (1 mg/ml). The reaction mixture was refluxed (110°C) under nitrogen for 24 hrs. After this reaction time both IR and 200 MHz ^{1}H-NMR analyses showed that the hydrosilylation reaction was complete. The white polymers were separated by precipitation in methanol, and purified by several reprecipitations from chloroform solutions into methanol and then dried under vacuum.

RESULTS AND DISCUSSION

The traditional pathway to synthesize low molecular weight liquid crystals implies the interconnection of two similar or dissimilar aromatic, trans-cyclohexane, bicyclooctane, etc., rings through a rigid interconnecting group. The interconnecting group should provide a linear and eventually planar conformation to the resulted compound. Therefore, again aromatic, trans-cyclohexane, bicyclooctane, trans-2,5-dioxane, -dithiane or -dioxathiane groups are preferred, although linking units containing multiple bonds about which freedom of rotation is restricted, as for example, $-C\equiv C-$, $-CH=N-$, $-N=N-$, $-(CH=CH)_n-$, $-CH=N-N=CH-$, etc. are frequently employed. This last group of multiple bonds can conjugate with the phenylene rings, enhancing the anisotropic polarizability. This function increases the molecular length and maintains rigidity. The ester group is also effective since resonance interactions confer double bond character on the C-O link restricting rotational motions. Although ethane and methyleneoxy units, can adopt a similar conformation with an ester group, they are flexible, and therefore, undergo free rotation leading to a number of different conformational isomers. Out of these conformational isomers, the one providing an extended structure, i.e., "anti" or "anti-periplanar" would certainly have to present similar properties with the structure constructed with an ester interconnecting units.

It was only recently, that the idea of replacing ester groups with methyleneoxy groups became pursued by organic chemists working in the field of low molecular weight liquid crystals (20-32). Methyleneoxy units were

successfull in stabilizing the mesophase, particularly when they were used to interconnect two cycloaliphatic units, or an aromatic and a cycloaliphatic unit. Low molecular weight liquid crystals containing a methyleneoxy unit in between two aromatic groups were reported only last year (27,32). In general, the replacement of an ester group with a flexible methyleneoxy group depresses the range of temperatures of the mesomorphic phases, and this is sometimes advantageous because these compounds become easily accessible for physical investigations. This is the case for the benzyl ethers of biphenyl derivatives (27, 32). On the other hand, the benzyl ethers of 2,6-disubstituted naphthalene derivatives which were reported so far, present only monotropic transitions, while the benzyl ethers of 4-cyanophenol undergo only virtual transitions (27).

To our knowledge, there are no reports in the literature concerning the use of benzyl ether based mesogens, in the synthesis of liquid crystalline polymers.

There are several different reasons which brought this class of mesogens to our attention. First, benzyl ether mesogens can be prepared by very simple synthetic procedures and are hydrolitically stable. Second, it is well documented that low molecular weight potential mesogens which do not exhibit liquid crystalline properties, give rise to liquid crystalline polymers when attached as side chains to polymer backbones. This would mean, that low molecular weight mesogens giving rise to either virtual or monotropic transitions, could lead to enantiotropic liquid crystalline side chain polymers. Third, this would represent a novel and simple class of liquid crystalline polymers based on mesogens presenting conformational isomerism, and at this time there is no information in the literature

concerning the influence of a mesomorphic phase on conformational isomerism or of conformational isomerism on the mesomorphic behavior. Therefore, this class of macromolecular liquid crystals could provide a simple model to study it.

Table II summarizes the thermal transitions of the monomeric compounds synthesized according to Scheme 1. IM presents a very narrow monotropic transition which could not be characterized, while IIM is crystalline only. The monomeric benzyl ethers of 4-cyano-4'-hydroxybiphenyl (IIIM) and of 4-methoxy-4'-hydroxy-biphenyl (IVM) present enantiotropic smectic mesophases. It has to be mentioned that IIIM presents solid state polymorphism i.e., a melting transition at 62°C followed by a solid state recrystallization and a second melting at 75°C, into a smectic mesophase.

The benzyl ether of 2-cyano-6-hydroxynaphthalene (VM) exhibits an unusual behavior which will be discussed based on the DSC scans presented in Figure 1. The first DSC heating scan of VM recrystallized from solution (Figure 1A) always presents only a melting transition at 99 °C. Optical polarized microscopy demonstrates that it melts into an isotropic liquid. All the cooling DSC scans (Figure 1D) are identical, indifferent of the previous heating scan thermal history, and present two exothermic transitions, at 80 and 44°C. Optical polarized microscopy reveals the formation of nematic droplets before 80°C suggesting an additional exotherm which cannot be observed by DSC. At 80 °C a smectic phase (focal conic texture) appears, and at 44°C the compound crystallizes. At the first sight we would tend to assume that these two liquid crystalline mesophases are monotropic. An investigation of the following heating scans performed after different cooling scans both by DSC and optical microscopy,

demonstrates that this is not the case. The second DSC heating scan (20°C/min) after a cooling scan performed with 20°C/min presents multiple transitions (Figure 1B). VM melts at 78°C into a very narrow smectic mesophase. At 79°C the smectic mesophase transforms into a nematic mesophase. The nematic mesophase undergo isotropization at 84°C. Up to this point there is a good agreement between the smectic and nematic mesophases observed both on the heating and cooling scans. Although optical microscopy performed with 10°C/min does not reveal additional transitions above 84°C, the DSC scan in Figure 1B shows an exotherm at 88°C and an endotherm at 99°C. Figure 1C presents the heating scan (20°C/min) of the sample quenched from the isotropic phase. This time, both the exotherm at 88°C and the endotherm at 98°C present higher enthalpy changes. At the same time it could be interesting to mention that the sum of all enthalpy changes of the endothermic transitions on the heating scans is almost constant and equal to that of the first scan, i.e., about 25 cal/g. When the quenched sample (from the isotropic phase in dry ice) is observed on the optical microscope it reveals in addition to melting, smectic, nematic and isotropic phases, the crystallization process at 88°C, followed by the melting process at 98°C. Therefore, the smectic and nematic mesophases of VM are virtual. To our knowledge this unique combination of liquid crystalline behavior combined with crystalline polymorphism has never been previously observed in low molecular weight or macromolecular liquid crystals, and it could be associated with different equilibria between the anti and gauche conformational isomers of the mesogens. Solids normally consist of a single conformer. For VM it could be the gauche one, which is less apt to give a mesomorphic phase than the anti one. Upon melting an equilibrium between

gauche and anti is established and therefore, the thermal history of the sample can control the entire behavior of this liquid crystal, through the gauche/anti ratio between the two conformers. Although several additional speculative explanations can be advanced at this time, a rigorous understanding of this behavior requires both x-ray diffraction and solid state NMR experiments. This work will be performed in our laboratory, and reported in due time.

Table III summarizes the thermal transitions and their corresponding thermodynamic parameters. The first important conclusion is that all polymers present enantiotropic liquid crystalline mesophases, despite the fact that some of the monomeric precursors are only crystalline or monotropic liquid crystalline compounds. These results support the assumption we made at the beginning of this work, i.e., that as in other cases of side chain liquid crystalline polymers, the polymer backbone will stabilize the liquid crystaline mesophase. It might be that in this case, the liquid crystalline mesophase could represent the driving force towards the stabilization of the anti conformation, which lead to an extended mesogen. Again, both x-ray and solid state NMR data are required to confirm this speculation.

All the synthesized polymers present smectic mesomorphism, and this is again an expected trend which is usually observed in going from monomeric to polymeric liquid crystals.

Interesting enough is the following observation. Results from several differernt laboratories reported that in most cases when long spacers like undecane were used, the side chain liquid crystalline polymer crystallizes below the liquid crystalline phase (13-16).

Figures 2 and 3 present several representative heating and cooling scans for the polymers IP and IIP. Liquid crystalline transitions are thermodynamically controlled while melting and crystallization are kinetically controlled. Therefore, we frequently discriminate between the two types of transitions by using different heating and cooling rates in the DSC experiments and comparing both the temperature and the corresponding thermodynamic parameters from the heating and cooling scans.

Based on these assumptions, the first endotherm on the heating scan of polymer IP (92°C) (Figure 2A) represents a melting into a smectic mesophase which undergoes isotropization at 119°C. On the cooling scan (Figure 2B) crystallization is more supercooled than the isotropization temperature. At the same time, the enthalpy change of crystallization is lower than that of melting, while the enthalpy change of isotropization does not differ from the heating to the cooling scan (Table III). The first heating scan for this sample is identical to the subsequent heating scans.

Figure 3 presents some representative DSC scans for the polymer IIP. This polymer undergoes an unusual behavior. The first heating scan (Figure 3A) presents a glass transtion temperature at 44°C and an endotherm at 101°C. All cooling scans present two exotherms (Figure 3B). The one at 93°C is due to isotropization, while the exotherm at 59°C is due to crystallization. Subsequent heating scans following cooling scans performed with 20°C present a melting into a smectic phase at 82°C and an isotropization at 99°C (Figure 3C). Evidence for the melting transition at 82°C does not come only from its supercooled crystallization and difference in its thermodynamic parameters (Table III) but also from the cold crystallization observed on a heating scan performed after quenching the

sample from isotropic phase (Figure 3D). It is interesting to mention that the enthalpy of the endotherm at 101°C from the first scan is higher than the sum of the two endotherms from the subsequent heating scans. A very careful analysis of the first and second heating scans shows that the two endotherms in the second scan cover the same range of temperature as the first heating scan. Therefore, in the first heating scan melting and isotropization temperatures are overlapped.

A similar characterization was performed for the polymers IIIP, IVP and VP. While IVP presents multiple liquid crystalline transitions (Table III), IIIP and VP present only glass transition temperatures, and a smectic mesophase. All three polymers give rise to anisotropic glasses on cooling below the glass transition temperature. Figure 4 presents representative heating (Figure 4A) and cooling (Figure 4B) scans for the polymer VP, to be compared with its monomeric precursor VM (Figure 1). While its monomeric precursor VM undergoes the complicated virtual transitions already discussed, the polymer VP presents a single enantiotropic smectic mesophase. This is an excellent example of polymer effects in side chain liquid crystalline polymers.

Acknowledgements

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Figure Captions

Figure 1: Normalized DSC thermograms for VM: a) A) first heating scan (20°C/min); B) third heating scan (20°C/min), after cooling with 20°C/min; b) C) fourth heating scan (20°C/min), after quenching from the isotropic phase, D) a representative cooling scan (20°C/min).

Figure 2: Normalized DSC thermograms (20°C/min) for IP: A) third heating scan; B) second cooling scan.

Figure 3: Normalized DSC thermograms for IIP: A) first heating scan (20°C/min); B) first cooling scan (20°C/min); C) second ~~cooling~~ heating scan (20°C/min); D) heating scan (20°C/min) after quenching from the isotropic phase.

Figure 4: Normalized DSC thermograms (20°C/min) for VP: A) second heating scan; B) second cooling scan.

Schemes

Scheme 1: Synthesis of benzyl ether monomers.

Scheme 2: Synthesis of liquid crystalline polysiloxanes.

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TABLE I

Characterization of Monomers

Compound	200 MHz ^{1}H - NMR ($CDCl_3$, δ, ppm)
IM	δ = 1.30 to 2.07 (m, 16H, -(CH_2)$_8$-), 3.96 (t, 2H, Ph -OCH_2-), 4.95 and 5.81 (m, 3H, -CH = CH_2), 5.01 (s, 2H, Ph -OCH_2- Ph), 6.88 to 7.58 (m, 8 aromatic protons).
IIM	δ = 1.31 to 2.07 (m, 16H, -(CH_2)$_8$-), 3.77 (s, 3H, -OCH_3), 3.96 (t, 2H, Ph -OCH_2-), 4.93 (s, 2H, Ph -OCH_2- Ph), 4.95 and 5.81 (m, 3M, -CH = CH_2), 6.80 - 7.34 (m, 8 aromatic protons).
IIIM	δ = 1.30 to 2.07 (m, 16H, -(CH_2)$_8$-), 3.95 (t, 2H, Ph -OCH_2), 4.94 and 5.80 (m, 3H, -CH = CH_2), 5.02 (s, 2H, Ph -OCH_2- Ph), 6.88 - 7.68 (m, 12 aromatic protons).
IVM	δ = 1.32 - 2.07 (m, 16H, -CH_2)$_8$-), 3.95 (t, 2H, Ph -OCH_2), 4.94 (m, 2H, = CH_2), 3.86 (s, 3H, -OCH_3), 3.97 (t, 2H, Ph -OCH_2-), 5.06 (s, 2H, Ph -OCH_2- Ph),, 4.97 and 5.84 (m, 3H, -CH = CH_2), 6.91 - 7.51 (m, 12 aromatic protons).
VM	δ = 1.31 - 2.08 (m, 16H, -(CH_2)$_8$-), 3.98 (t, 2H, Ph -OCH_2), 4.97 and 5.83 (m, 3H, -CH = CH_2), 5.04 (s, 2H, Ph -OCH_2- Ph), 6.88 - 7.7 (m, 10 aromatic protons).

TABLE II

Thermal Transitions and Thermodynamic *Parameters of Monomers*

	Thermal Transitions (^{o}C) and Thermodynamic Parameters: ΔH (Kcal/mole); ΔS(cal/mole ^{o}K)																	
	Heating										Cooling							
Monomer Type	Tm	ΔHm/ΔSm	T_1	$\Delta H_1/\Delta S_1$	T_2	$\Delta H_2/\Delta S_2$	T_r	ΔHr/ΔSr	Ti	$\Delta H_i/\Delta S_i$	T_c	$\Delta H_c/\Delta H_c$	T_1	$\Delta H_1/\Delta S_1$	T_2	$\Delta H_2/\Delta S_2$	T_i	$\Delta H_1/\Delta S_1$
IM	84	11.10/31.09	--	--	--	--	--	--	--	--	58	10.54[a]/--	--	--	--	--	59	--
II ~~IIM~~	83	12.93/36.32	--	--	--	--	--	--	--	--	69	12.48/36.49	--	--	--	--	--	--
III ~~IIIM~~	62	2.18/6.51	75[b]	4.60/13.21	--	--	--	--	147	1.45/3.45	37.5	5.43[c]/--	41.5	--	--	--	143	1.52/3.65
IVM	119	2.17/5.54	146	--	--	--	--	--	151.5	10.32[d]/--	106	1.99/5.25	136	--	140	--	146	9.86[e]/--
VM	78	7.33[f]/--	79	--	84	0.14/0.39	88[g]	--	99[b]	2.59/6.99	44	6.88/21.7	--	--	--	--	80	1.06/3.00

a) Overlapped transitions: $\Delta Hc = \Delta H_c + \Delta Hi$; b) Second melting; c) Overlapped transitions: $\Delta H_c = \Delta H_c + \Delta H_1$; d) Overlapped transitions: $\Delta H_i = \Delta H_i + \Delta H_1$; e) Overlapped transitions: $\Delta H_i = \Delta H_i + \Delta H_i + \Delta H_2$; f) Overlapped transitions: $\Delta H_m = \Delta H_m + \Delta H_1$; g) Recrystallization.

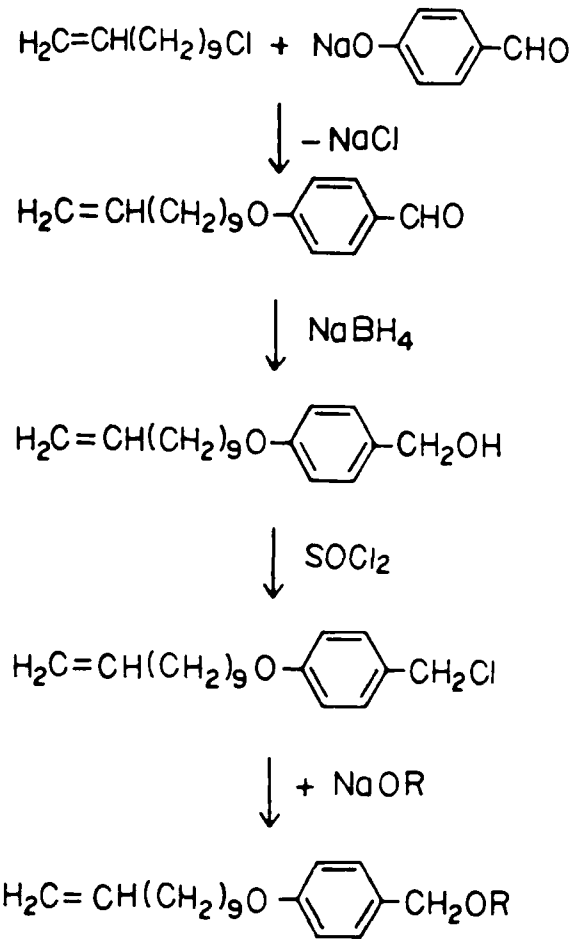
TABLE III

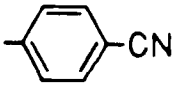
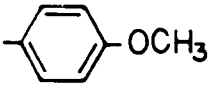
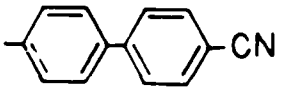
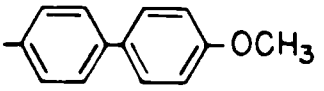
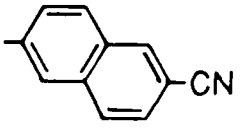
Thermal Transitions and Thermodynamic Parameters of Polymers

Polymer Type	Thermal Transitions (^{o}C) and Thermodynamic Parameters: ΔH (Kcal/mru); ΔS (cal/mru ^{o}K)*																
	Heating									Cooling							
	T_g	T_1	$\Delta H_1/\Delta S_1$	T_2	$\Delta H_2/\Delta S_2$	T_3	$\Delta H_3/\Delta S_3$	T_1	$\Delta H_1/\Delta S_1$	T_1	$\Delta H_1/\Delta S_1$	T_2	$\Delta H_2/\Delta S_2$	T_3	$\Delta H_3/\Delta S_3$	T_1	$\Delta H_1/\Delta S_1$
IP	30.5	--	--	--	--	92[a]	2.43/6.66	119	0.87/2.22	--	--	--	--	69.5[b]	1.89/5.52	112	0.89/2.31
IIP	44	--	--	--	--	82[a]	2.29/6.45	99	1.53/4.11	--	--	--	--	59[b]	1.94/5.84	93	1.57/4.29
IIIP	15	--	--	--	--	--	--	217	1.08/2.20	--	--	--	--	--	--	197	1.08/2.30
IVP	63	146	0.41/0.98	182	0.51/1.12	228	--	235	2.17[c]/-	135	0.39/0.96	170	0.48/1.08	219	--	226	2.14[c]/-
VP	19	--	--	--	--	--	--	163.5	0.75/1.72	--	--	--	--	--	--	157	0.75/1.74

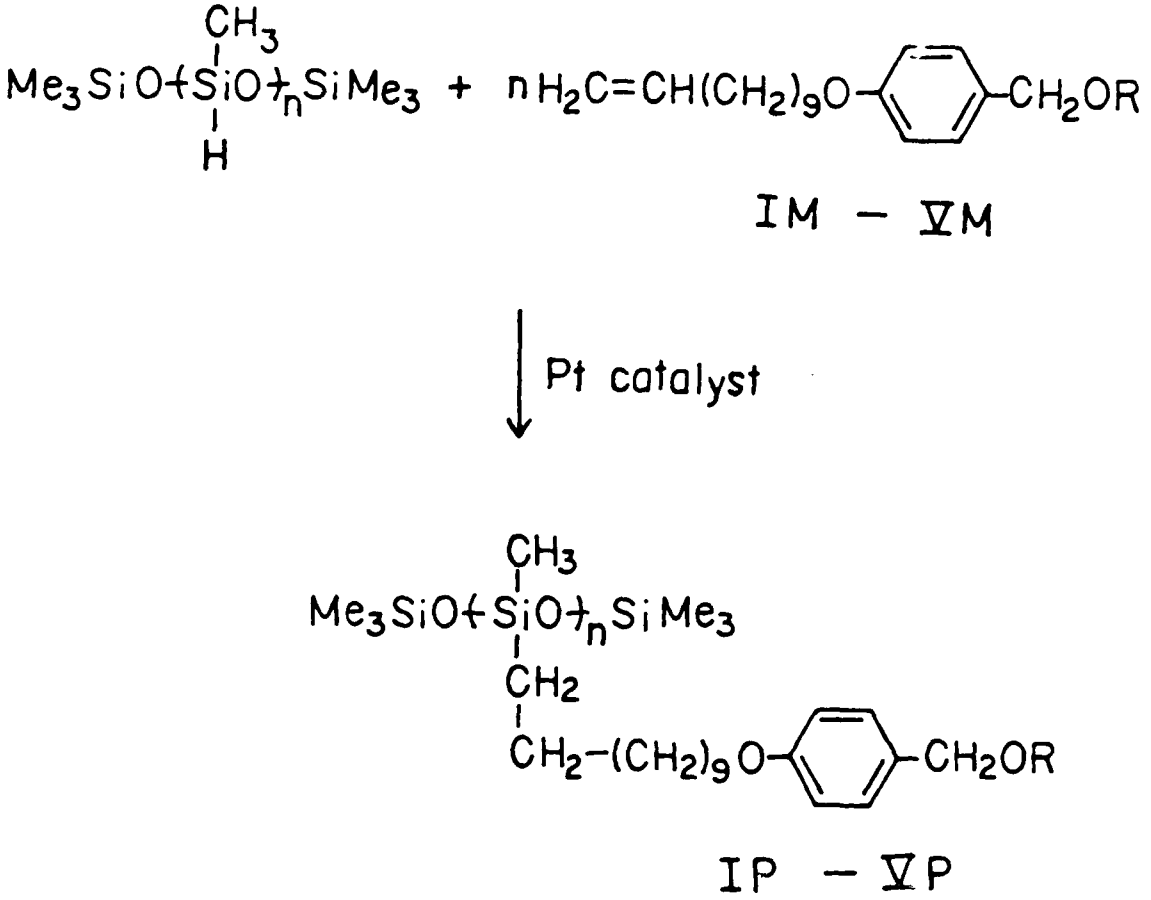
* mru = mole repeat unit

a) melting; b) crystallization; c) overlapped transitions: $\Delta H_1 = \Delta H_3 + \Delta H_1$



MONOMERS	R
IM	
IIM	
IIIM	
IVM	
VM	

Scheme 1


Me3SiO[Si(CH3)(H)O]nSiMe3 + n H2C=CH(CH2)9O-C6H4-CH2OR
IM – VM
Pt catalyst
Me3SiO[Si(CH3)(CH2-(CH2)9O-C6H4-CH2OR)O]nSiMe3
IP – VP

Scheme 2

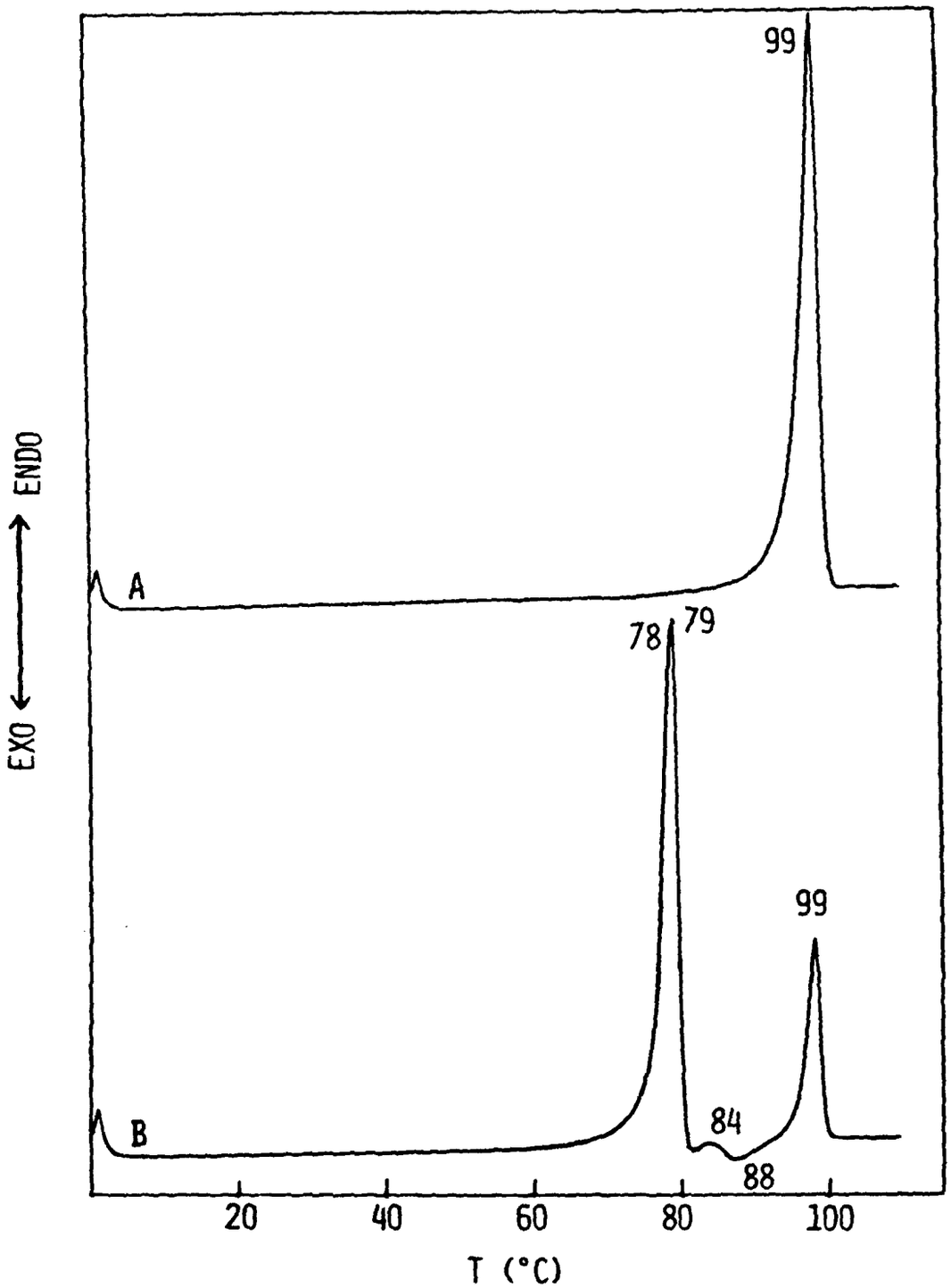


Fig 1a

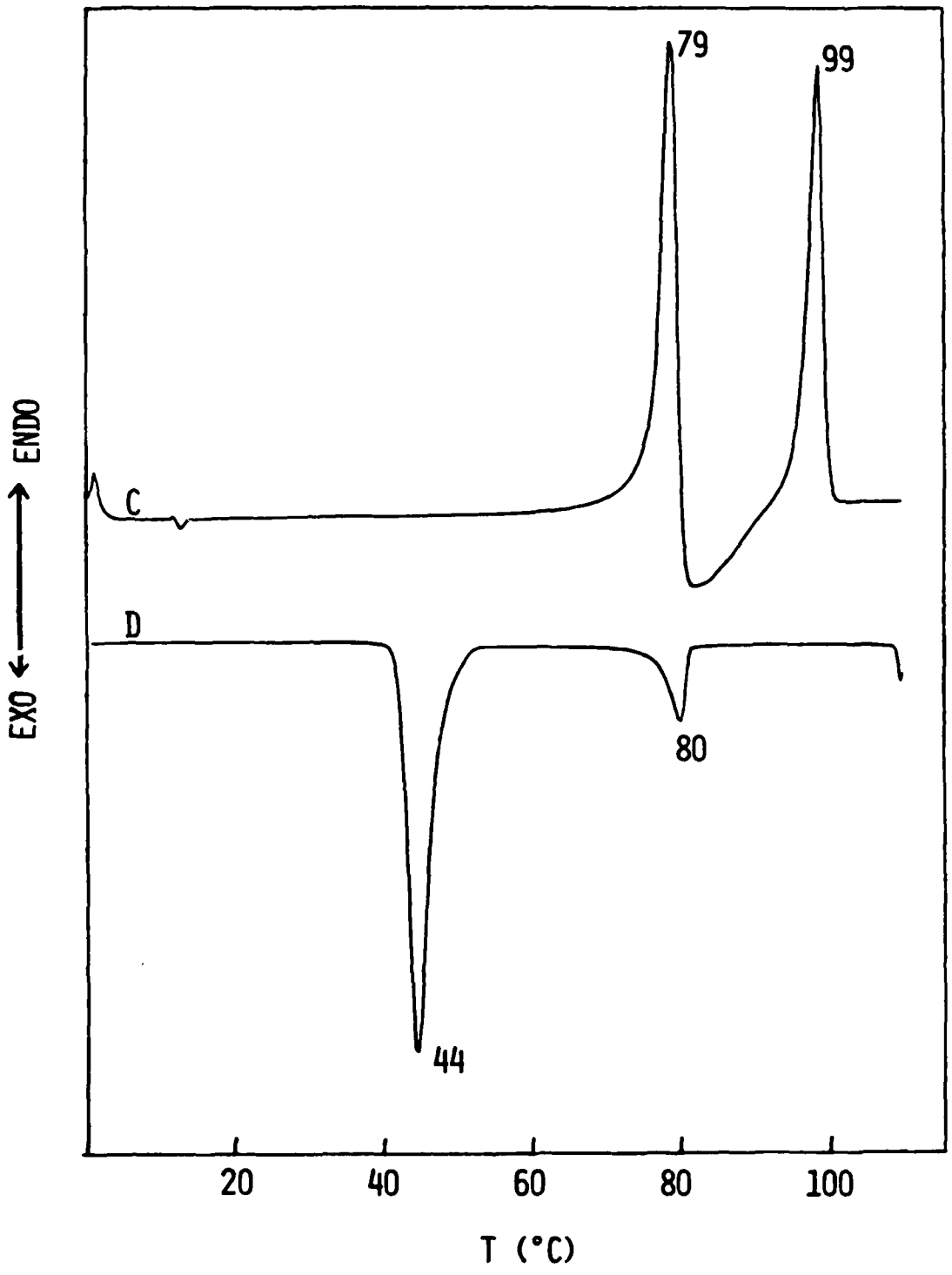


Fig 16

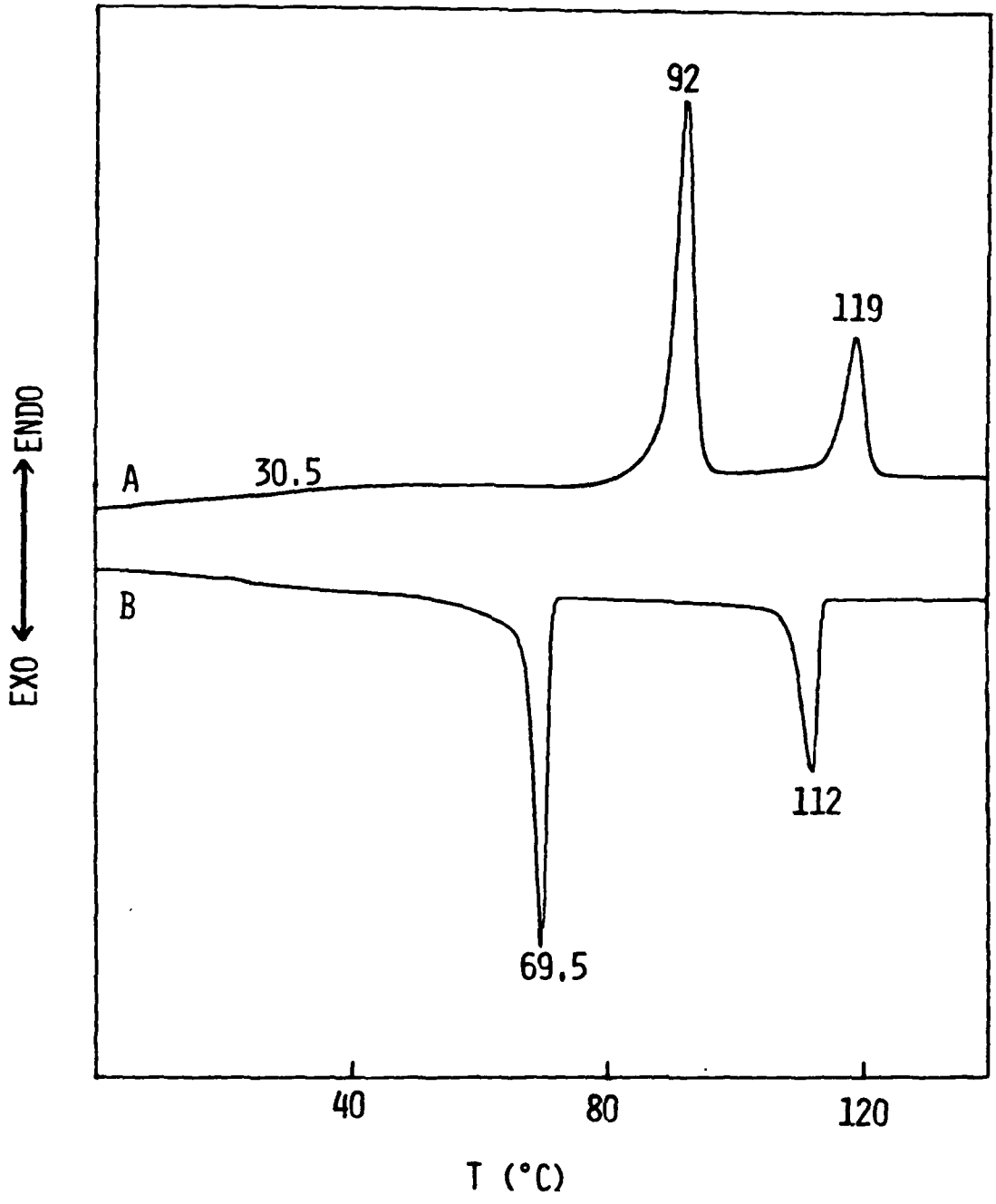


Fig. 2

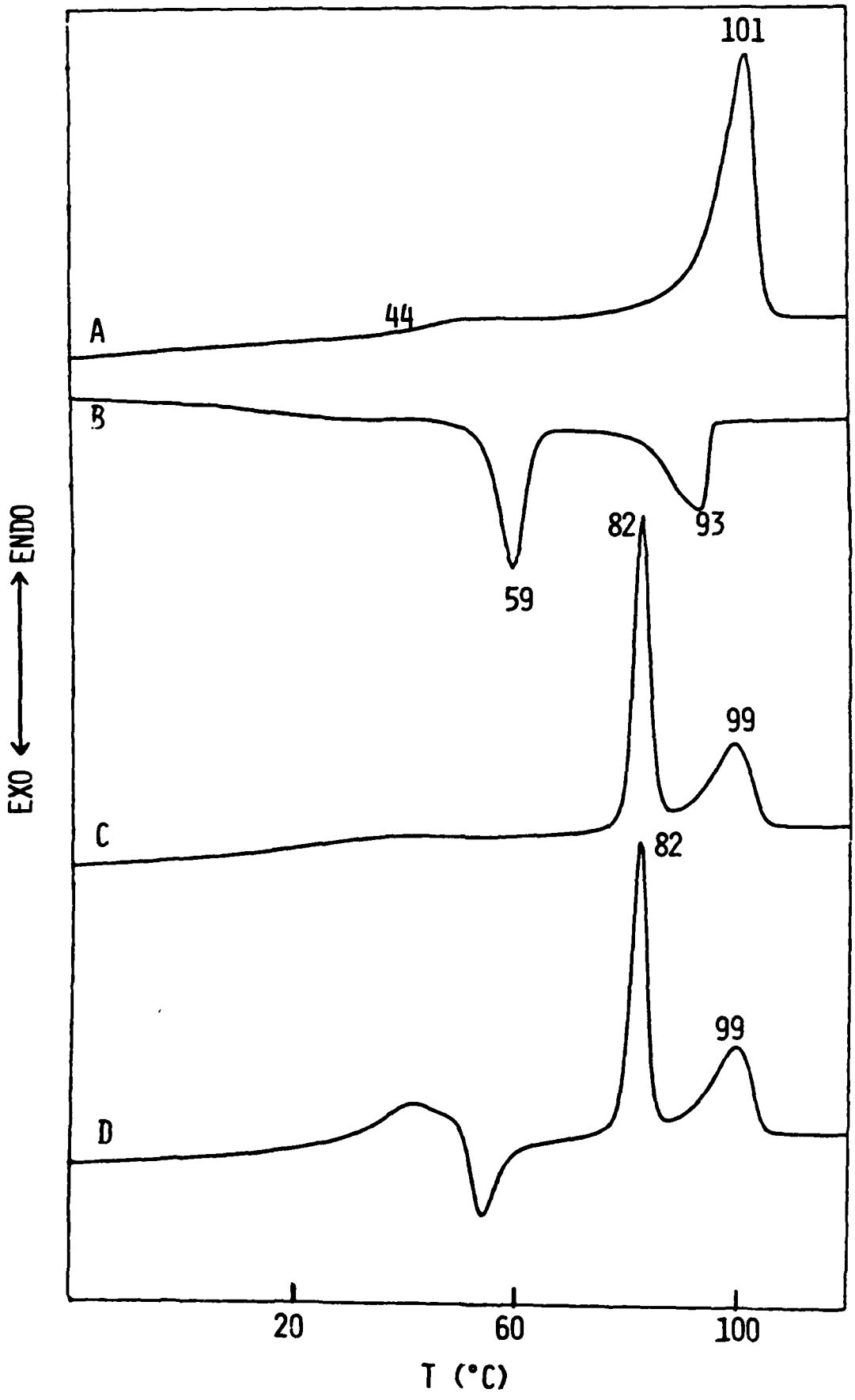


Fig.3

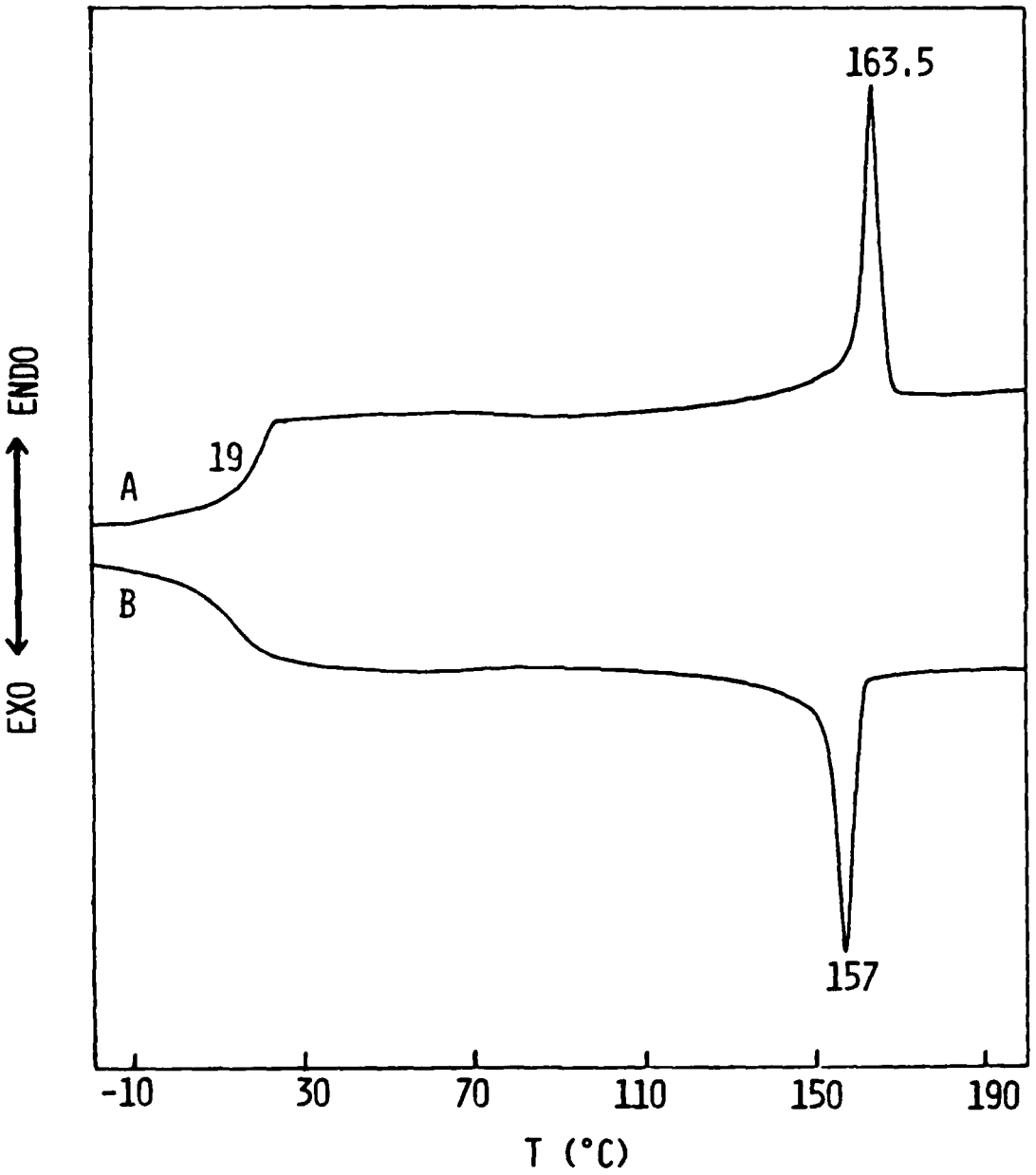


Fig 4

END

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DTIC